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REACTION OF THIANTHRENE CATION RADICAL WITH ALCOHOLS: CYCLOHEXANOLS

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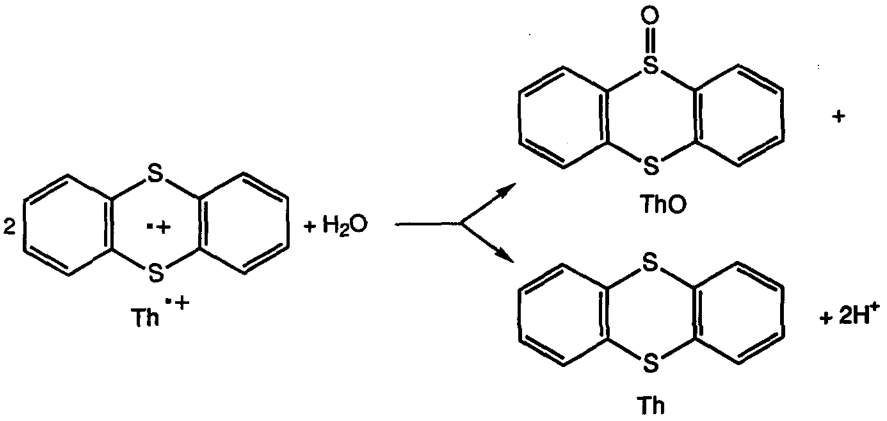
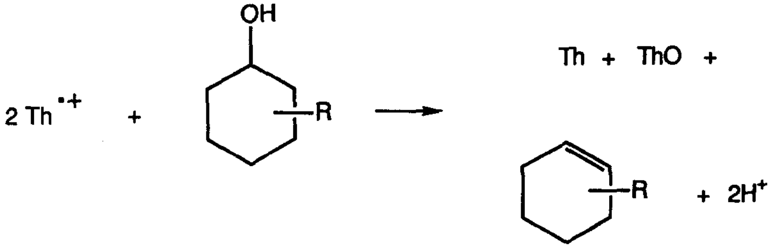
Abstract: Cyclohexanol (1), 4-methylcyclohexanol (2), 4-tert-butylcyclohexanol (3), cis-2-methyl- (4) and trans-2-methylcyclohexanol (5) reacted cleanly with thianthrene cation radical perchlorate ($Th^{\cdot+}ClO_4^-$) in the presence of 2,6-di-tert-butyl-4-methylpyridine (DTBMP). The alcohols were converted quantitatively into cyclohexenes, while $Th^{\cdot+}$ was converted quantitatively into thianthrene (Th) and thianthrene 5-oxide (ThO). The oxygen atom of ThO came from the alcohol, as was demonstrated with the use of [^{18}O]cyclohexanol.

One of the most intensely, mechanistically studied reactions of $Th^{\cdot+}$ is that with water, the stoichiometry of which is shown in eq. 1.[1] In contrast, no analogous study of reactions of $Th^{\cdot+}$ with alcohols has been reported. We have begun such a study and report here our first results, with cyclohexanols. Cyclohexenes were formed quantitatively, according to the stoichiometry of eq. 2. Reactions were carried out at room temperature in acetonitrile solution with an excess of the alcohol and in the presence of a hindered base (DTBMP) in order to prevent acid-catalyzed dehydration of the alcohol. Quantitative results from gc measurements are given in Tables 1 and 2. They show equivalent amounts of ThO and cycloalkene, as is expected of the stoichiometry of eq. 2. Also shown is the equivalence, as expected, of the amounts of Th and ThO. That the amount of Th is always a little higher than of ThO may be attributable to the inclusion of small amounts of Th in the preparation of solid $Th^{\cdot+}ClO_4^-$.[2]

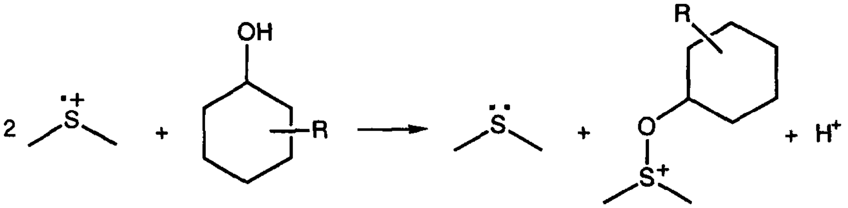
It is evident from the relatively high oxidation potentials (> 2V) of alcohols[3] and that of Th (approx. 1.3 V vs SCE[4]) that the reaction of $Th^{\cdot+}$ with these alcohols cannot originate in an oxidation reaction. Instead, in analogy with the water reaction,[1] complexation of an alcohol with $Th^{\cdot+}$ must occur, and lead eventually to an unstable alkoxysulfonium ion, as summarized schematically in eq. 3, from which ene products are derived. Elimination of the alkene from the alkoxysulfonium ion occurs either by an E1 or E2 route. Guidance as to


2
Th
+ H2O
ThO
+
Th
+ 2H+

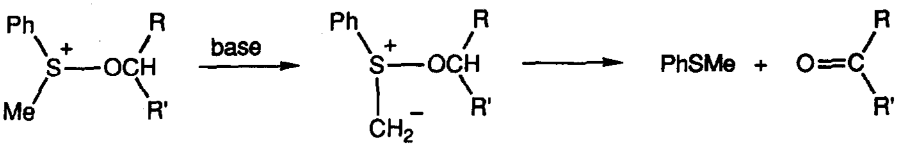
(1)


2 Th
+
OH
R
Th + ThO +
R
+ 2H+

(2)


2
S
+
OH
R
S
+
R
O
S+
+ H+

(3)


Ph
S
Me
OCH
R
R'
base
Ph
S
OCH
R
R'
CH2
PhSMe
+
O=C
R
R'

(4)

these routes can be obtained from comparisons of the results from 4 and 5 with data in the literature. For example, Martin's dehydration of 4 and 5 with the complex-forming sulfurane, $(C_6H_5)_2S(OR_F)_2$, gave, by clearly E2 routes, 100% of 3-methylcyclohexene from 5 (trans) and predominantly 1-methylcyclohexene (3:1 ratio) from 4 (cis).[5] On the other hand, methanolysis of the tosylates of 4 and 5 gave 99% of 1-methylcyclohexene from 4 (cis) and predominantly 3-methylcyclohexene (3:1 mixture) from 5 (trans). Methyl cyclohexyl ethers formed in the methanolyses indicated that E1/SN1 occurred principally with 4, but E2/SN2 and some E1/SN1 with 5.[6] Our reactions, in contrast, appear to have a lot of E1 character. This is evident with 5 which gave 65% of 1-methylcyclohexene, and 4 which gave almost quantitative formation of 1-methylcyclohexene.

In order to be certain that the oxygen in ThO is derived from the alcohol, rather than from H_2O added in workup, reaction with $[^{18}O]$cyclohexanol[7] was carried out. The ^{18}O contents of the starting cyclohexanol and ThO, isolated from reaction, were measured by mass spectrometry, (M + 2)/M, and were in accord with eq. 2.

In connection with our comment on the inability of $Th^{\cdot+}$ to oxidize alcohols, Shono and coworkers have reported the catalytic effect of $PhSMe^{\cdot+}$ in the anodic oxidation of secondary alcohols to ketones.[8] For example, 2-methylcyclohexanol was converted into 2-methylcyclohexanone (85%) in the presence of PhSMe and 2,6-lutidine. Formation of the ketones was attributed to the intramolecular deomposition of an alkoxysulfonium ylide, eq. 4. Phenyl methyl sulfoxide was obtained, but its formation was attributed to reaction of water with $PhSMe^{\cdot+}$ or $PhSMe^{2+}$. In the light of our results, the $PhSMe^{\cdot+}$ mediated reaction may need to be re-examined.

Table 1. Products[a] of Reaction[b] of $Th^{\cdot+}ClO_4^-$ with Cyclohexanol (1), 4-Methyl- (2) and 4-*tert*-Butylcyclohexanol(3)

Alcohol	$[Th^{\cdot+}ClO_4^-]_0$	Th	ThO	ene[c]	ene/ThO
1	81.2	41.0	40.4	39.9	0.988
$[^{18}O]1$	80.3	42.2	36.9	36.9	1.00
2[d]	81.2	40.8	38.2	37.5	0.982
3[d]	80.6	40.8	39.5	39.8	1.01

[a] $[Th^{\cdot+}ClO_4^-]_0$ and products in mmol x 10^2. [b] Approx. 0.8 mmol of $Th^{\cdot+}ClO_4^-$ in 20 mL of dry CH_3CN under argon, to which was added by syringe either a solution of 0.8 mmol of DTBMP in 0.25-0.30 mL of alcohol or a solution of these reagents in 1 mL of CH_3CN. The numbers of runs averaged were four (1), two ($[^{18}O]1$), three (2), and two (3). Products were assayed by gc. [c] cyclohexene, 4-Me-, and 4-*t*-Bucyclohexene, as appropriate. [d] A mixture of isomers.

Table 2. Products[a] of Reaction of $Th^{\cdot+}ClO_4^-$ with *cis*- (4) and *trans*-2-Methylcyclohexanol (5)

Alcohol	$[Th^{\cdot+}]_0$	Th	ThO	1-ene	3-ene	enes/ThO
4[b]	80.5	39.5	38.1	37.7	0.85	1.01
5[c]	80.3	40.6	39.3	25.7	13.4	0.995

[a] See footnotes, Table 1. [b] Average of two runs. [c] Average of four runs.

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